

Site-competition epitaxy for n-type and p-type dopant control in CVD SiC epilayers

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Abstract: The use of site-competition epitaxy, which is based on intentional variation of the Si/C ratio during epitaxy, has now been reproduced in numerous national and international laboratories. However, previous reports have only considered dopant incorporation control for epitaxy on the Si-face 6H-SiC(0001) substrates. Presented in this paper is the extension of this technique for control of phosphorous incorporation and also a comparison of controlled doping on C-face 6H-SiC(0001) versus Si-face 6H-SiC(0001) substrates for aluminum, boron, nitrogen, and phosphorous.

1. Introduction

Site-competition epitaxy is an advancement in SiC crystal growth which has been reported for control of nitrogen, aluminum, and boron dopant incorporation for the chemical vapor deposition (CVD) of SiC(0001) Si-face epilayers [1,2]. The use of this technique has also been reproduced on SiC(0001) Si-face substrates in other laboratories using either propane[3,4] or methane[5] in atmospheric and low pressure CVD systems, as well as reproduced [6] on SiC(1210) a-face substrates. Control of dopant incorporation is accomplished by varying the Si/C ratio within the growth reactor to effectively exclude or enhance a particular dopant atom from either a Si-lattice-site (Si-site) or C-lattice-site (C-site) of the growing SiC epilayer. As previously reported [1], the proposed mechanism for site-competition epitaxy on 6H-SiC(0001) Si-face substrates is based on the experimental evidence that Al dopant incorporation is inversely proportional to the Si/C ratio, whereas the N dopant incorporation is directly proportional to the Si/C ratio within the reactor during epilayer growth.

This proposed mechanism is also based on previous reports that dopant atoms occupy specific lattice sites of the SiC crystal structure, with N occupying C-sites and Al residing in Si-sites[7]. It was also reported that boron may be amphoteric in nature, possibly occupying both SiC crystal lattice-sites[8,9], which could preclude the successful use of site-competition epitaxy. However, results of successfully implementing site-competition epitaxy for control of B-doping support that B preferentially occupies the Si-site along with a significant amount of hole-passivating hydrogen which is also incorporated during B-doped epilayer growth[10].

These previous investigations of site-competition epitaxy for SiC CVD of 6H-, 4H-, and 3C/6H-SiC polytypes included only Si-face and a-face SiC substrates, but not C-face substrates. Reported in this paper are the results of site-competition epitaxy experiments to additionally control phosphorous as an n-type dopant, as well as results from using site-competition epitaxy on 6H-SiC(0001) C-face as compared to 4H- and 6H-SiC(0001) Si-face off-axis substrates.

2. Experimental

The 6H-SiC epilayers were grown on commercially available n-type 6H- and 4H-(0001)SiC Si-face and C-face 6H-(0001)SiC boule-derived wafers[11] in an atmospheric pressure CVD system[12,13], with a typical growth rate of 3-4 $\mu\text{m/h}$. The SiC substrates were precleaned using a standard degreasing solution, followed by immersion in boiling sulfuric acid for 10 minutes, with a final deionized-water rinse and then dried with filtered nitrogen. The cleaned substrates were placed onto a SiC-coated graphite susceptor and then loaded into a water-cooled fused-silica reactor using a fused-silica-carrier. The samples were heated via the RF-coupled susceptor which was temperature controlled at 1450°C using an optical pyrometer. Silane (gas cylinder containing 3% in H_2) and propane (3% in H_2) were used as the sources for SiC epilayer growth, whereas 90 sccm flow of ultrapure hydrogen chloride gas in a 3 sLpm flow of hydrogen was used during a 1350°C in situ etch just prior to epilayer growth. All gases were mass flow controlled, including the ultra-pure hydrogen carrier-gas which was purified by using a heated-palladium diffusion cell. The epilayers were doped n-type by the addition of phosphine (200 ppm PH_3 in H_2) or nitrogen (0.1% N_2 in H_2) and p-type by the addition of diborane (100 ppm B_2H_6 in H_2) or trimethylaluminum (bubbler configuration) into the reactor during epilayer growth. Secondary ion mass spectrometry (SIMS) was performed[14] using a CAMECA IMS-4f double-focussing, magnetic sector ion microanalyzer. Cesium bombardment was used for determination of hydrogen, boron, phosphorous, and nitrogen atomic concentration profiles by using the detector in a negative secondary ion detection mode to monitor H^- , P^- and the diatomic species $\text{B}(\text{C})^-$, $\text{N}(\text{C})^-$, respectively.

3. Results

For the 6H- and 4H-SiC(0001) Si-face samples, nitrogen dopant incorporation into Si-face epilayers is directly related to the Si/C ratio within the reactor. The Si/C ratio was purposely varied by changing only the propane flow during the epilayer growth experiment while both the silane and nitrogen flows were maintained constant. The SIMS depth profiles indicate that the atomic nitrogen concentration decreased as the propane flow was increased during epilayer growth, as previously reported[1]. This is consistent with an increased amount of carbon outcompeting the nitrogen for vacant carbon-sites (C-sites) of the SiC crystal lattice on the growing SiC epilayer surface.

Phosphorous (P) dopant incorporation was determined to be inversely related to the Si/C ratio as displayed in Figure 1. As the propane flow was decreased, while maintaining a constant silane (20 sccm) and phosphine (100 sccm) flow, the SIMS determined P incorporation also decreased within the Si-face 6H-SiC epilayer. These changes in P incorporation with variation in the Si/C ratio are consistent with the P atom occupying the silicon-sites (Si-sites) of the SiC crystal lattice. As the propane flow is increased, the amount of vacant Si-sites increases which could allow enhanced P incorporation into the SiC epilayer.

The p-type doping on the Si-face was accomplished using trimethylaluminum (TMA) for aluminum (Al) and diborane for boron (B) doping. SIMS analysis revealed that the Al dopant incorporation was inversely related to the Si/C ratio used during epilayer growth on both 6H and 4H Si-face substrates. In Figure 2, the SIMS determined Al incorporation increased as the

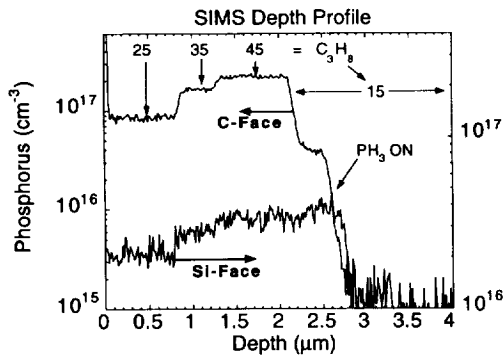


Figure 1 SIMS depth profile of a phosphorus-doped epilayer simultaneously grown on a 6H-SiC(0001) Si-face versus a C-face substrate. Initially, the propane flow is constant then the phosphine flow is established. Then both the silane and phosphine flows are maintained constant while the propane flow is varied (stepwise).

propane flow was increased and also when the silane flow was decreased within the CVD reactor, which clearly demonstrates competition between Si and Al for the Si-sites on the growing Si-face 6H-SiC epilayer.

Similarly, boron doping is also directly related to the Si/C ratio, as shown in Figure 3. In addition to boron incorporation a significant concentration of hole-passivating hydrogen is also incorporated during the growth of the B-doped epilayer. As previously reported, SIMS analysis confirms that the hydrogen can be removed from the epilayer by annealing at 1700°C in argon for 30 minutes which results in a 3X increase in the mercury-probed net hole concentration for these B-doped epilayers [10].

In general, p-type doping of epilayers grown on C-face 6H-SiC(0001) samples was similar to that determined for the Si-face substrates. Both Al and B dopant incorporation on the C-face exhibited a similar dependence on the Si/C ratio, as previously described for the Si-face substrates. However, both Al and B incorporation were markedly less efficient on the C-face substrates when compared to Si-face substrates that were doped during the same growth run. For Al doped C-face epilayers, the SIMS determined Al dopant incorporation was approximately 50X less than that of the corresponding Si-face epilayer. Similarly, B-doped C-face epilayers also exhibited a 50X lower atomic B concentration compared to simultaneously B-doped Si-face epilayers. As was previously reported for B-doped Si-face epilayers[10], hydrogen was also detected for the B-doped C-face epilayers, where the variation in the SIMS determined H concentration profile paralleled that of the SIMS determined, stepped B-concentration profile.

Site-competition epitaxy had a pronounced effect for control of P dopant incorporation on both C-face and Si-face epilayers. As the propane flow was decreased, the P incorporation also decreased (see Figure 1). As the silane flow was increased and then decreased, the P incorporation decreased then increased, respectively (not shown). It is believed that P is competing with Si for available Si-sites on the growing C-face SiC epilayer.

In contrast, N doped epilayers on the 6H-SiC(0001) C-face revealed a more complex response of N incorporation with a change in the Si/C ratio. As shown in Figure 4, the SIMS determined atomic N concentration contained in the C-face epilayer initially decreases as the unintentional background nitrogen in the CVD system slowly decreases during the start of epilayer growth. The N incorporation then decreases as the propane flow is decreased (from 50 to 15 sccm), which is directly opposite to the site-competition effect for the Si-face epilayers. It is important to note that the (C-face) N incorporation decreases despite the simultaneous

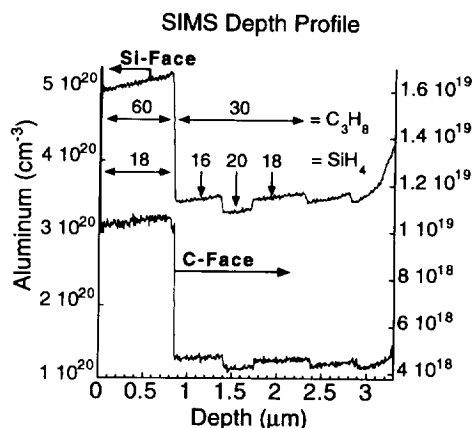


Figure 2 SIMS depth profile of an aluminum-doped epilayer simultaneously grown on a 6H-SiC(0001) Si-face versus a C-face substrate. As the silane flow is varied during a constant propane flow, the Al is outcompeted by Si for available Si-sites. As the propane flow is increased to 60 sccm, Al incorporation increases because of the increase in available Si-sites.

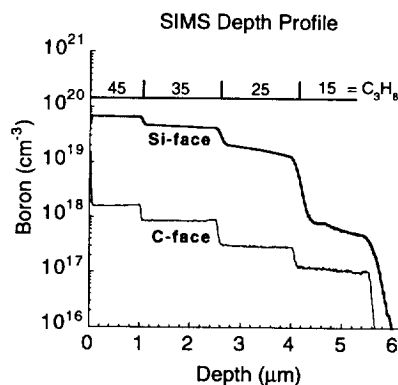


Figure 3 SIMS depth profile of a boron-doped Si-face versus C-face 6H-SiC(0001) epilayer from the same growth run. The silane and diborane were maintained constant as the propane flow was varied (sccm) during the epilayer growth.

introduction of 100 sccm of nitrogen into the CVD reactor, which demonstrates the dominant effect of the Si/C ratio on dopant incorporation. As the propane flow is subsequently increased stepwise, the C-face N incorporation initially increases from $3 \times 10^{18} \text{ cm}^{-3}$ to $6 \times 10^{19} \text{ cm}^{-3}$ and then decreases stepwise to $3 \times 10^{19} \text{ cm}^{-3}$, coinciding with the stepwise increases in propane flow.

4. Discussion

In general, Si-face site-competition for 6H-SiC(0001) was similar to that of the 4H-SiC(0001) substrates. The site-competition effect for Al doping is consistent with Al substitutionally occupying the Si-sites of the SiC lattice for epilayers grown on both Si-face and C-face 6H-SiC(0001) substrates. A similar site-competition effect was obtained in which B is also believed to mainly occupy the Si-sites for B doping on both faces. As shown in Figure 2, Al incorporation is more efficient on the Si-face compared to the C-face, which is consistent with a previously reported doping study using photoluminescence[15]. For n-type doping with phosphorus, the site-competition effect is most consistent with the P atom mainly occupying the Si-sites. This effect can be rationalized by considering that the lattice site occupied by each dopant atom is partly determined by the size of the dopant atom as compared to the size of the Si or C atom. Specifically, the non-polar covalent radii for the elements of interest are: Si (1.17\AA); C (0.77\AA); Al (1.26\AA); B (0.82\AA); P (1.10\AA); and N (0.74\AA) [16]. Using atomic size as a first approximation (i.e. by neglecting chemical bonding arguments), both Al and P should substitute for Si and not for C in the SiC lattice, which is consistent with our experimental results. The more closely matched atomic size of B to C suggests that B should substitute mainly for C in the C-sites, which is in direct conflict with experimental evidence[10,17]. However, a considerable amount of H is simultaneously incorporated into the growing B doped epilayer and therefore a "B-H" complex could be considered as the substitutional species. In this case, a "B-H" species would have a size (1.10\AA) more closely matched with that of Si (1.17\AA) and therefore should occupy a Si-site, in agreement with the experimental results. Because this is only a first approximation, it does not imply that B substitutes exclusively into the Si-sites but rather that the Si-site substitution is favored because of the larger effective size of the proposed "B-H" species.

The N doping on the Si-face is consistent with the site-competition mechanism, in which the relatively small N atoms compete with C atoms for available C-sites. However, the results from using site-competition epitaxy on the C-face are not as easily understood. SIMS analysis of N-doped C-face epilayers indicate that N-incorporation initially increases with increasing propane flow. This increase in N-incorporation for the C-face reaches a maximum and subsequent increases in propane flow result in a decrease in N-incorporation, which is similar to site-competition for Si-face epilayers.

This can be understood by considering the relatively small size of the N atom (0.74\AA) which would allow possible substitution into both the C-site and the Si-site. For example, in

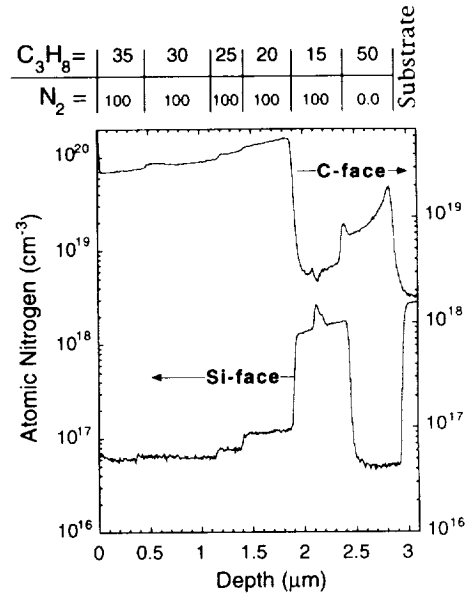


Figure 4 SIMS depth profile of a C-face compared to a Si-face 6H SiC(0001) N-doped epilayer grown during the same growth run. Note that the (C-face) N incorporation decreases, as the propane flow decreases (from 50 to 15), despite the simultaneous introduction of 100 sccm of nitrogen into the CVD reactor, which demonstrates the dominant effect of the Si/C ratio on dopant incorporation. Subsequent propane flows were varied, from 15 to 35 (sccm), to change the Si/C ratio and effectively control N incorporation with constant nitrogen and silane flows (sccm).

Figure 4 the Si-face substrates have very low unintentional (i.e. $N_2 = 0.0$ sccm) N-dopant incorporation when grown in excess propane ($C_3H_8 = 50$ sccm) at the start of the epilayer growth. In contrast, the C-face 6H-SiC epilayer initially demonstrated a large amount of N incorporation (also at $C_3H_8 = 50$ sccm). The propane flow was then decreased ($C_3H_8 = 15$ sccm) resulting in a decreased N incorporation for the C-face despite the simultaneous introduction of nitrogen (100 sccm). This is consistent with N mainly occupying the Si-sites on the C-face. As the propane flow was then increased, as shown in Figure 4 ($C_3H_8 = 20$ sccm), the N-dopant incorporation increases for the C-face which is consistent with N substituting into Si-sites. Further stepwise increases in propane flow (in excess of 20 sccm) reverses this effect for the C-face, resulting in a stepwise decrease in N-dopant incorporation (for $C_3H_8 = 25$ to 35 sccm) which is consistent with the excess C competing with N for the C-sites.

These results of using site-competition on the C-face are consistent with the N-dopant atoms preferentially substituting into the Si-sites, with a smaller but significant contribution from N incorporation into the C-sites. It is proposed that as the propane concentration is increased from $C_3H_8 = 15$ to 20 sccm, the N incorporation decreases in the C-sites but simultaneously increases (to a much larger extent) into the Si-sites, resulting in a net increase in N-dopant incorporation for the C-face epilayer as shown in Figure 4. At this propane flow ($C_3H_8 = 20$ sccm), most of the available Si-sites may have become occupied such that further increases in propane flow does not appreciably increase N-incorporation into the Si-sites. As the propane flow is then increased further, the decreased N incorporation in the C-sites becomes apparent from the net decrease in atomic N as determined by SIMS depth profiling ($C_3H_8 = 25$ to 35 sccm).

5. Conclusion

Site-competition epitaxy was successfully used for p-type and n-type dopant control on both the Si-face and C-face of 6H-SiC(0001) off-axis substrates. The doping results for the C-face provides supporting evidence that the site-competition effect is highly dependent on the SiC polarity but not significantly affected by the polytype. The results for both the 6H- and 4H-SiC Si-face samples were similar whereas the 6H-SiC C-face samples yielded significantly different results, specifically for N-doped epilayers. It also becomes obvious, in comparing the results from simultaneous growth of N-doped epilayers on the C-face and Si-face, that the site-competition mechanism is highly dependent on the surface structure of the SiC substrate and relatively less dependent on gas phase interactions.

For p-type doping, the Al and B dopant incorporation increased as the Si/C ratio was decreased by increasing the propane flow on both polar faces. Similarly, the P dopant incorporation also increased on both the Si-face and C-face as the Si/C ratio was intentionally decreased from either a decrease in the silane flow or increase in the flow of propane during epilayer growth. This is consistent with the P, Al, and B competing with Si for the available Si-sites.

The site preference for each dopant can be partially understood by considering their atomic sizes relative to the sizes of Si (Si-site) and C (C-site). Here, the P and Al are clearly too large for incorporation into the C-site without changing the lattice spacing, whereas B needs further explanation. Because a significant amount of H is incorporated with B we must consider the relative size of B to be of a "B-H" complex. For this situation, the effective size of the "B-H" complex is also too large and will not easily fit into the C-sites without significantly altering the SiC lattice dimensions. In contrast, the relatively small size of the N dopant atom theoretically allows incorporation into either of the lattice sites. Therefore, it is now believed that N doping on the Si-face results in N incorporation into both the Si-site and the C-site, with N mainly incorporating into the C-site. In contrast, for N doping on the C-face, N mainly incorporates into the Si-sites with relatively less incorporation into the C-sites. Therefore, the originally proposed site-competition mechanism must be modified to account for N dopant incorporation into both Si-sites and C-sites, in which the degree of incorporation for each site (i.e. Si-site versus C-site) is dependent upon the growth surface polarity. This more detailed mechanism is under investigation and will be described in a future publication.

The doping of SiC epilayers is influenced by many factors during the CVD epilayer growth

process and needs to be fully understood to ensure controlled, reproducible doping of epilayers for reliable SiC device operation. Therefore, work is continuing in order to further elucidate the mechanism and scope of site-competition epitaxy and to determine the dominant factors which influence the doping of CVD SiC epilayers.

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7. References

- [1] Larkin D J, Neudeck P G, Powell J A and Matus L G 1994 *Appl. Phys. Lett.* **65** 1659-1661
- [2] Larkin D J, Neudeck P G, Powell J A and Matus L G 1994 *Silicon Carbide and Related Materials: Proceedings of the Fifth International Conference* *Institute of Physics Conference Series* **137** (Bristol, United Kingdom: IOP Publishing) 51-54
- [3] Karmann S, Cioccio L D, Blanchard B, Ouisse T, Muiyard D and Jaussaud C 1995 *Materials Science and Engineering B* **B29** 134-137
- [4] Rupp R, Lanig P, Schorner R, Dohnke K-O, Volkl J and Stephani D 1995 *6th International Conference on Silicon Carbide and Related Materials* (Kyoto, Japan)
- [5] Tischler M A 1995 personal communication
- [6] Burk A A Jr. et al 1993 presented at International Conference on Silicon Carbide and Related Materials (Washington, DC)
- [7] Davis R F and Glass J T. "The Growth and Characterization of Silicon Carbide and Diamond for Microelectronic Applications." Trans. North Carolina State University, NCSU. *Advances in Solid-State Chemistry*. Ed. C R A Catlow. London: JAI Press Ltd., 1991. 2: 1-111.
- [8] Zubatov A G, Zaritskii I M, Lukin S N, Mokhov E N and Stepanov V G 1985 *Sov. Phys. Solid State* **27** 197
- [9] Veinger A I, Vodakov G A, Kozlov Y I, Lomakina G A, Mokhov E I, Oding V G and Sokolov V I 1980 *Sov. Tech. Phys. Lett.* **6** 566
- [10] Larkin D J, Sridhara S G, Devaty R P and Choyke W J 1995 *Journal of Electronic Materials* **24** 289-294
- [11] Cree Research, Inc. (Durham, NC)
- [12] Powell J A, Matus L G and Kuczumski M A 1987 *J. Electrochem. Soc.* **134** 1558-1565
- [13] Powell J A, Larkin D J, Matus L G, Choyke W J, Bradshaw J L, Henderson L, Yoganathan M, Yang J and Pirouz P 1990 *Appl. Phys. Lett.* **56** 1442-1444
- [14] Charles Evans & Associates (Redwood City, CA)
- [15] Clemen L L, Devaty R P, Macmillan M F, Choyke W J, Burk A A Jr., Barrett D L, Hobgood H M, Larkin D J and Powell J A 1993 presented at International Conference on Silicon Carbide and Related Materials (Washington, DC)
- [16] Purcell K F and Kotz J C 1977 *Book Inorganic Chemistry* (Philadelphia, PA: W. B. Saunders Co.)
- [17] Reinke J, Muller R, Feege M, Greulich-Weber S and Spaeth J-M 1994 *Materials Science Forum* **143-147** 63-68